

PARTIAL TRANSLATION OF JP 49-33353 B

Title of the Invention: Method for Preparing Aqueous
Dispersion
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Detailed description of the invention

The present invention relates to a method for preparing an aqueous dispersion of a reactive copolymer.

To improve the stability of an emulsion or a property, such as the adhesiveness or water resistance, of a film obtained from the emulsion, a method for production of an emulsion of copolymers of ethylene and vinyl acetate in the presence of a polymeric compound other than ethylene and vinyl acetate is known. JP 39-19547 B discloses a method for production of a coating with good water resistance or an aqueous emulsion for processing papers or textiles by copolymerizing ethylene and vinyl acetate in the presence of acrylic acid, methacrylic acid, fumaric acid, etc. without use of general emulsifiers. JP 42-22692 B discloses a method for production of a well-stabilized emulsion having a high solid content and imparting water resistance to paper, textiles or leather by polymerizing a three-component system of, for example, ethylene, vinyl acetate, acrylic acid with specific emulsifiers of $\text{HO}(\text{C}_2\text{H}_4\text{O})_a$, $(\text{C}_3\text{H}_6\text{O})_b$, $(\text{C}_2\text{H}_4\text{O})_c \cdot \text{H}$, wherein a represents an integer between 30 and 90; b , one between 10 and 60; and c , one between 30 and 90.

The present invention relates to a method for stably preparing an emulsion of a reactive copolymer mainly composed of ethylene and vinyl acetate by copolymerizing polymeric compounds having reactive functional groups in the presence of a given amount of an inorganic salt in an aqueous medium.

A copolymer emulsion which has a stable reactivity and contains few coarse particles and in which an increase in the viscosity of the polymerization system is prevented is obtained by adding an inorganic salt to an extent that an emulsifier do not precipitate in an aqueous polymerization system comprising ethylene, vinyl acetate and a water-soluble polymeric compound generating a polymer which is water-soluble or remarkably swells in water. It is considered that the water-soluble polymer obtained by the addition of the inorganic salt is mostly deposited from the aqueous medium, because the dehydrated water-soluble polymer decreases the water-solubility thereof and absorbs the emulsifier to become a stable particle of the emulsion, and swelling of the water-soluble polymer is prevented.

The copolymer emulsions in the present invention include emulsions mainly based on copolymers comprising 40 to 94% by weight of ethylene, 5 to 60% by weight of vinyl acetate and 1 to 20% by weight of water-soluble polymerizable compound generating a water-soluble polymer, such as a compound selected from acrylic acid, methacrylic acid, acrylamide, methacrylamide, N-methylolacrylamide, N-methylol methacrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate and the like, or a mixture of

these compounds. The emulsions also includes ones partially containing water-soluble polymers inevitably generated because of the polymerization activity of the compounds involved.

The inorganic salt in the present invention is a material usually called an "inorganic salt", and is selected from a hydrochloride, a nitrate, a sulfate or a carbonate of Li, Na, K, Mg, Ca, Zn, Al, Sn(II), Pb(II), etc., which has a solubility of at least 1 part relative to 100 parts of water at room temperature, has no color when dissolved in water, and does not react chemically with water to generate another compound. The inorganic salt is not an inorganic compound generally used as a catalyst or a buffering agent. The salts include LiCl, NaCl, Na₂SO₄, NaCO₃, K₂SO₄, MgCl₂, SnCl₂, etc., and mixtures of two or more of them. The amount of the inorganic salt used in the aqueous medium, which does not contain monomers for polymerization, must be 0.5 to 5% by weight.

The emulsifier in the present invention may be a common anionic surfactant, which is exemplified by a sulfate ester salt of a higher alcohol, such as laural alcohol, an alkylbenzene sulfonate, such as sodium salt of dodecylbenzene sulfonic acid, or an alkyl naphthalenesulfonate, or a combination of such an anionic surfactant and a nonionic surfactant, such as polyoxyethylene alkyl ether, polyoxyethylene alkyl phenol ether, polyoxyethylene sorbitan fatty acid ester, or oxyethylene-oxypropylene block polymer. A preferable amount of emulsifier used is about 2 to 8% in an aqueous

medium excluding monomers.

As a catalyst, a water-soluble radical-forming agent, such as t-butyl peroxide, hydrogen peroxide, potassium persulfate, sodium persulfate, or ammonium persulfate, or a well-known redox system, is used. The polymerization temperature depends on the initiator used, but is generally 100°C or less, preferably 50 to 70°C.

The ethylene pressure in the present invention does not directly affect the operation of the added inorganic salt, but in terms of the mechanical properties of the films and other products obtained from the emulsion, it should be about at least several tens of atmospheres, or preferably not less than 100 atmospheres. There is no upper limit on the pressure, but in terms of equipment or costs, the practical limit is about 500 atmospheres.

When the emulsion obtained by the present invention is used as a binder for treating nonwoven fabric, using the emulsion with methylol melamine, glyoxal or an ethyleneurea-based cross-linking agent produces a material insoluble to a solvent used for dry cleaning using Perclene, etc. In the case of the emulsion used for a coating or adhesive, by the introduction of a polar group, the emulsion has increased adhesiveness and shows marked enhancement in water and solvent resistance. Adjusting the pH of the resulting emulsion discretionarily changes the viscosity of the same, making the emulsion suitable for a binder for flocky processing.

Example 1

A one-liter stainless-steel autoclave equipped with a magnetic stirrer was charged with the following materials:

Water	400 g
Oxyethylene-oxypropylene block polymer	18.75 g
Sodium laural sulfate	11.25 g
Sodium hydrogenphosphate	1.5 g
Ammonium persulfate	2.0 g
Vinyl acetate	150 g
Methacrylic acid	20 g
Sodium sulfate	5 g

The autoclave was fully charged with nitrogen gas, was then injected with 182 g of ethylene, and heated to 60°C. Additional ethylene raised the inner pressure of the autoclave to 300 kg/cm² at 60°C. Polymerization was carried out for seven hours while maintaining a constant inner pressure of 300 kg/cm². After the polymerization, unreacted materials were purged, and the content was removed. The mass of ethylene added from the initiation of polymerization to the end was 86 g. The emulsion obtained weighed 680 g and was a uniform aqueous dispersion containing no coarse particles and having a viscosity, as measured by a B-type viscometer, of 130 CPS. The emulsion had a solid concentration of 41% by weight, of solid content. The polymer contained 39% by weight of vinyl acetate and 6.5% by weight of methacrylic acid. The emulsion was dried on glass plates at room temperature, and treated with heat for 5 minutes at 150°C to obtain a film having a tensile strength of 40 kg/cm² and an elongation of 900%. Further, 8 parts of a solution of 50% by weight of methylol melamine in water and 0.5 parts by weight of

ammonium chloride were added to 100 parts of the emulsion to prepare a mixture. A film obtained by treating the mixture with heat for 4 minutes at 150°C had a tensile strength of 62 kg/cm² and an elongation of 800%, and did not swell or dissolve during immersion in tricrene for 24 hours at room temperature.

Examples 2 to 12

Examples 2 to 12 repeated Example 1, with varying raw materials, types and amounts of emulsifiers, and the amounts and kinds of other materials, and at a different ethylene pressure (150 kg/cm², constant value).

The following table summarizes the results.

Example	Mass of vinyl acetate (g)	Mass of ethylene glycol (g)	Mass of emulsifiers (g)	Third monomers (g)	Inorganic salts (g)	Mass of catalyst (g)	Polymerization time (hrs)	Mass of emulsion product (g)	Solid concentration (wt %)	Emulsion viscosity (cPS)	Polymer constitution (wt %)	Film properties (I)			Film properties (II)		
												tensile strength (kg/cm ²)	elongation (%)	solvent resistance	tensile strength (kg/cm ²)	elongation (%)	solvent resistance
Example 2	145	168	74	A 18	B 12	Na ₂ SO ₄ 15	13	680	42.3	73	46	3.7	20	625	35	350	A
" 3	"	169	"	"	"	"	10	602	41.4	150	43	3.1	3.6	375	18	200	B
" 4	140	171	70	"	"	"	18	"	43.0	35	41	4.4	15	700	43	525	A
" 5	145	169	76	2-HBA	"	7.0	8	665	40.6	150	47	2.3	9.4	650	21	550	B
" 6	150	166	74	"	"	Na ₂ SO ₄ 20	13	689	42.5	140	44	5.8	39	1050	54	825	A
" 7	"	165	72	"	"	NaCl 7.0	"	640	38.8	119	48	5.9	"	"	"	"	A
" 8	"	"	74	"	"	NaCl 5.0	"	693	42.7	135	43	5.3	"	"	"	"	A
" 9	"	166	"	"	"	Na ₂ SO ₄ 3.0	"	659	40.1	192	46	"	"	"	"	"	A
" 10	"	163	76	"	"	Na ₂ SO ₄ 3.0	"	664	40.5	261	"	"	"	"	"	"	A
" 11	"	164	74	"	"	"	"	652	39.7	93	47	5.6	"	"	"	"	A
" 12	"	159	72	"	"	"	18	673	41.5	184	"	7.9	"	"	"	"	A
Comparative examples 1	150	163	76	"	"	None	13	675	41.9	4470	High viscosity			"	"	"	A
" 2	"	165	74	"	"	"	15	673	41.5	6920	Exothermic abnormality and blocked state			"	"	"	A
" 3	"	"	40	"	"	"	5	547	"	"	Monomers were not emulsified.			"	"	"	A
" 4	"	162	0	"	"	Na ₂ SO ₄ 25	8	Trace	"	"	Monomers were not emulsified.			"	"	"	A
" 5	"	163	70	"	"	None	10	650	"	"	Destruction			"	"	"	A

Note

1. Common condition:

Mass of water 400 g
 Sodium hydrogenphosphate 1.5 g
 Catalyst Ammonium persulfate
 Reaction temperature 60°C
 Pressure 150 kg/cm² (constant)

2. Emulsifier A: Oxethylene-oxypropylene block-polymer (AOEKA pluronic F-68 manufactured by Asahi Denka Co., Ltd.)

Emulsifier B: Sodium lauryl sulfate ester (EMAL #0 manufactured by KAO Corporation)

3. Film properties (I): The obtained emulsions were dried on the glass plate, and treated with heat at 150°C for 5 minutes, and tested.

The tensile strength test conditions were a chuck distance of 4 cm and a tensile speed of 300 mm/min.

The solvent resistance of the film was evaluated by testing the swelling degree and the solubility thereof after the film was immersed in tricene for 24 hours at room temperature. The evaluation mark D means that the film was mostly dissolved, C means that the film was remarkably swollen but the considerable insoluble portions left, B means little swelling of the film, but the film was dissolvable to some degree, and A means that the film remained almost fully intact.

Film properties (II): A film obtained by further adding methylol melamine as in the manner of Example 1 was tested as for film properties (I).

4. The third monomer: AAC Acrylic acid
 MAAC Metacrylic acid
 AAm Acrylamide
 N-MAAm N-methylol acrylamide
 2-HEMA 2-hydroxyethyl methacrylate

Claim

1. A method for preparing a reactive and stable aqueous dispersion characterized in that, during preparation of an aqueous dispersion of copolymer comprising 40 to 94% by weight of ethylene, 5 to 60% by weight of vinyl acetate and 1 to 20% by weight of a soluble polymeric compound generating a polymer which is soluble in water or has a swelling property in an aqueous medium, 0.5 to 5% by weight of an inorganic metal salt other than a catalyst and a buffering agent is added separately from the catalyst or the buffering agent to an emulsifier aqueous solution containing no monomers at the commencement of polymerization.